Thermal Stabilization of Cellulose Materials Using Pyrolysis with Catalytic Conversion

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Abstract

The operation and maintenance of processes in the nuclear complex result in the generation of a variety of cellulose materials that are contaminated with actinides. In an attempt to minimize the safety and environmental problems associated with storing and disposing of these materials, the nuclear complex has been investing considerable resources to stabilize these materials and to recover the actinides. In this effort, a pyrolysis process with catalytic conversion has been developed to achieve this end. In this process, the cellulose materials are decomposed in a high-temperature chemically inert environment, and the resulting decomposition products are volatilized and removed from the actinides as an off-gas. The remaining material is significantly reduced in both mass and volume, and is in a form suitable for the convenient recovery of the actinides. The process also incorporates a catalytic conversion step to oxidize the decomposition products. This step eliminates the formation of any potential waste streams, and effectively mitigates any flammable or combustible hazard that would compromise the safety of the process. The process also has been ergonomically designed and optimized for glovebox operations. The process has recently been installed in the Plutonium Facility at Los Alamos National Laboratory and is expected to be in operation in the immediate future.

Assessment of Problem

- The nuclear complex generates a variety of cellulose materials that are contaminated with actinides.
  - Cheese cloth rags
  - Wood
  - Paper

Assessment of Problem

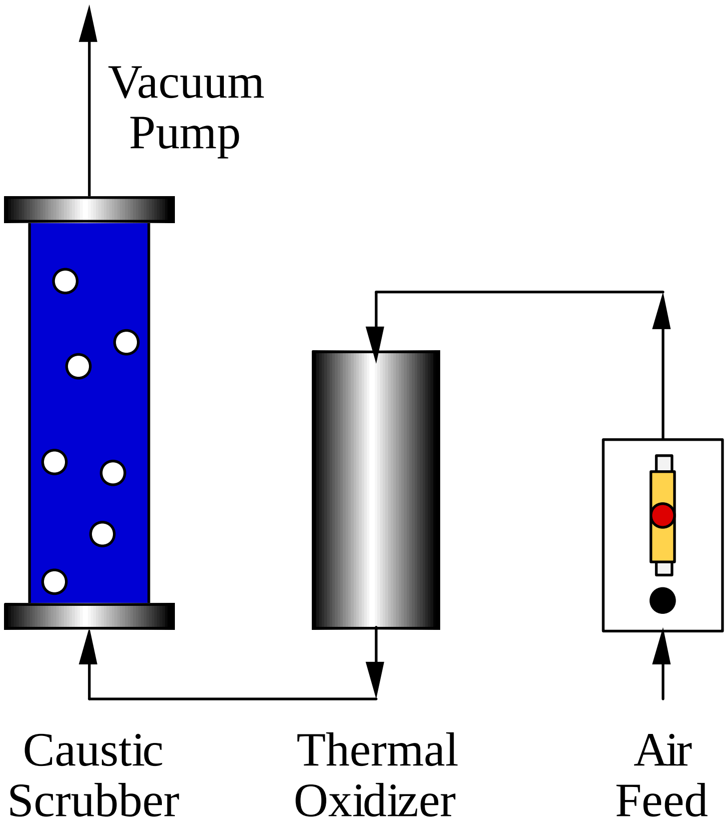
- Long-term storage of the cellulose materials is not an option.
  - Radiolytic decomposition of the cellulose forms products that could pressurize the storage containers.
  - Storing the cellulose is a very inefficient utilization of valuable storage space.

Assessment of Problem

- Shipping and disposing of the cellulose materials is not desirable.
  - Actinide concentrations in the cellulose are often too high to allow for direct disposal.
  - Packaging and shipping materials for disposal is expensive.
  - Radiolytic decomposition of the cellulose forms products that could pressurize shipping containers.
  - Certain actinide isotopes are too valuable to be discarded.

The Original Cellulose Stabilization Process

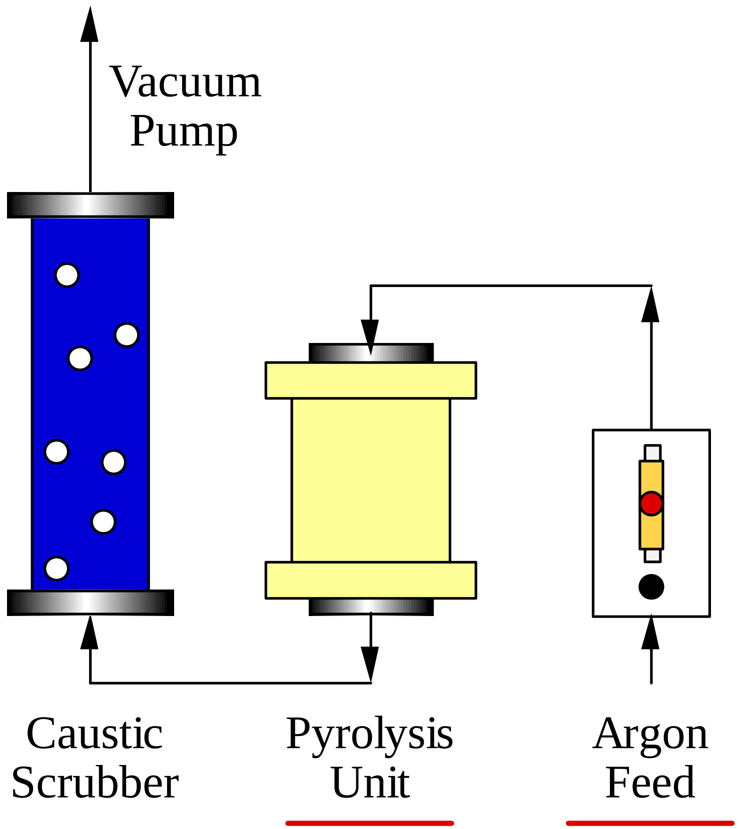
Direct Thermal Oxidation



- The cellulose was placed in a reactor, and ignited in an air environment. The cellulose was oxidized directly to CO_2 and H_2O.
- This process was discontinued in 1990 due to the moratorium on incineration.

The Present Cellulose Stabilization Process

Thermal Decomposition



- The process was change from incineration to pyrolysis by replacing the air feed with an argon feed, and by modifying the reactor design.
- The cellulose is brought to an elevated temperature in an argon environment. The cellulose decomposes into a series of compounds that are passed to a caustic scrubber.
- This process has been in operation since 1990.

The Present Cellulose Stabilization Process

- The cellulose is placed in the pyrolysis reactor. The feed and effluent lines are attached.
- Electrical resistance heating elements heat the reactor and its contents under a flow of argon.

The Present Cellulose Stabilization Process

- Problems with the present cellulose stabilization process:
  - > Loss of actinides
  - > Generation of waste streams
  - > Maintenance of the pyrolysis unit
  - > Maintenance of the scrubber

The Present Cellulose Stabilization Process

- Problem #1: Loss of actinides
  - Actinides are entrained by the off-gas stream leaving the pyrolysis reactor, are trapped by the scrubber solution, and are subsequently discarded.
  - Certain actinide isotopes are rare, and are deemed valuable based on programmatic needs. The loss of these actinide isotopes is a loss of a very precious resource.

The Present Cellulose Stabilization Process

- Problem #2: Generation of waste streams
  - > Actinides are entrained by the off-gas stream leaving the pyrolysis reactor, and are trapped by the scrubber.
  - > Many of the off-gas compounds from the pyrolysis reactor condense in the scrubber.
  - > A caustic scrubber solution containing actinides, hydrocarbons, and other compounds is generated by the process. Periodically, the solution must be discarded as a waste stream.

The Present Cellulose Stabilization Process

- Problem #3: Maintenance of the pyrolysis unit
  - The electrical resistance heating elements frequently short out, and must be replaced.
  - Repairing the heating elements of the pyrolysis unit increases the potential for radiation exposure and contamination.
  - The damaged heating elements must be discarded. This represents an additional waste stream generated by the process.

The Present Cellulose Stabilization Process

- Problem #4: Maintenance of the scrubber
  - > The off-gas compounds from the pyrolysis reactor foul the scrubber. Periodically, the scrubber must be cleaned with steam.
  - > Cleaning the scrubber increases the potential for radiation exposure and contamination.
  - > Cleaning the scrubber generates an additional waste stream which must be discarded.

The Pyrolysis Process with Catalytic Conversion

- The above process was designed and built by LANL under the DNFSB 91-4 R&D Project to stabilize polycubes at Hanford Site.

The Pyrolysis Process with Catalytic Conversion

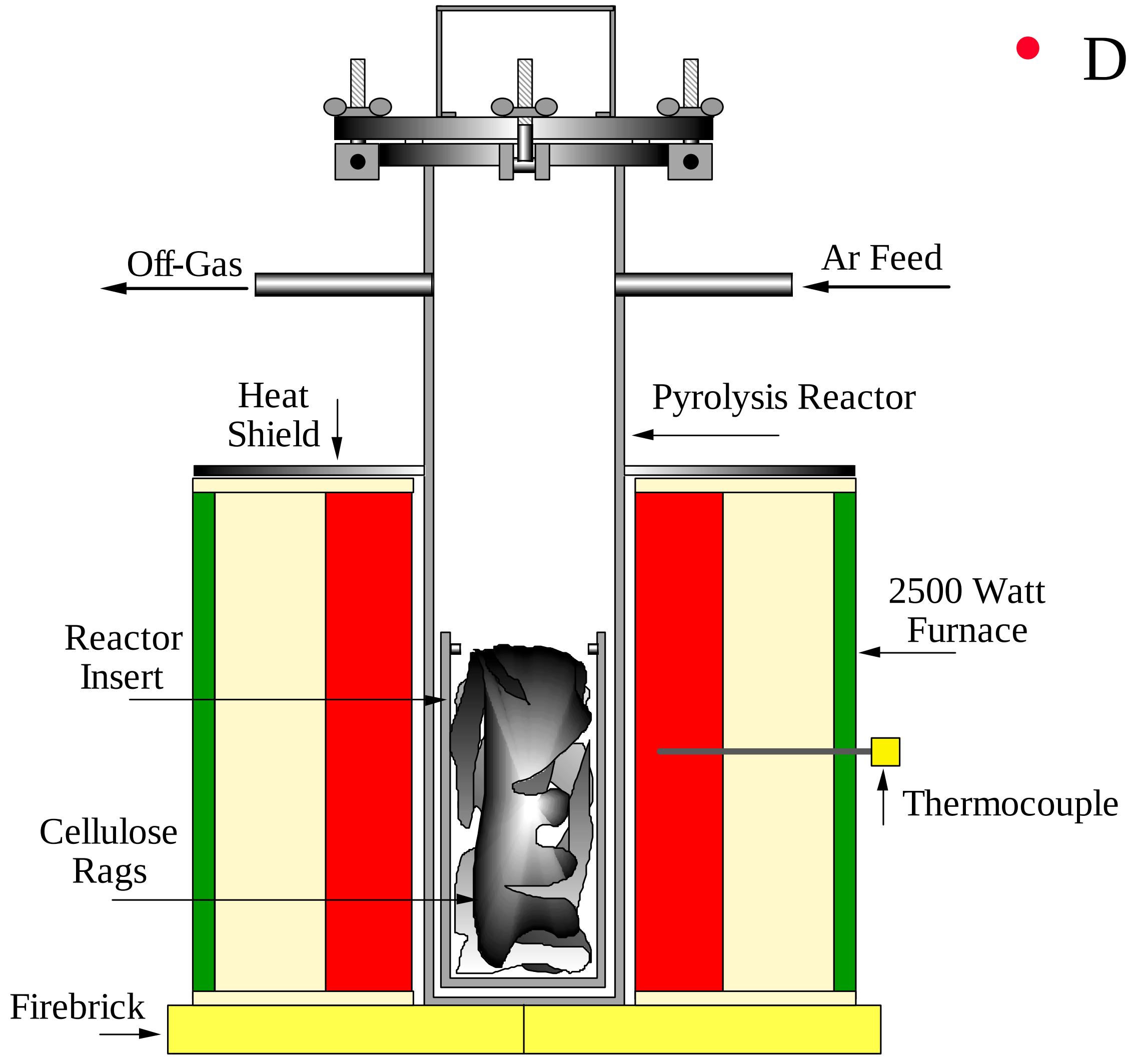
Stabilization of Polycubes

- Benefits of process:
  - It transforms polymers into a form suitable for actinide recovery.
  - It oxidizes the off-gas compounds to CO_2 and H_2O.
  - It is ergonomically designed for glovebox environments.
  - It requires only minimal maintenance.

The Pyrolysis Process with Catalytic Conversion

- The goals of this stabilization effort:
  - To optimize the pyrolysis process with catalytic conversion to stabilize cellulose materials.
  - To implement the process in the Plutonium Facility at Los Alamos National Laboratory.
  - To put the process in operation to stabilize cellulose materials, and by doing so, reduce or eliminate the problems associated with the present cellulose stabilization process.

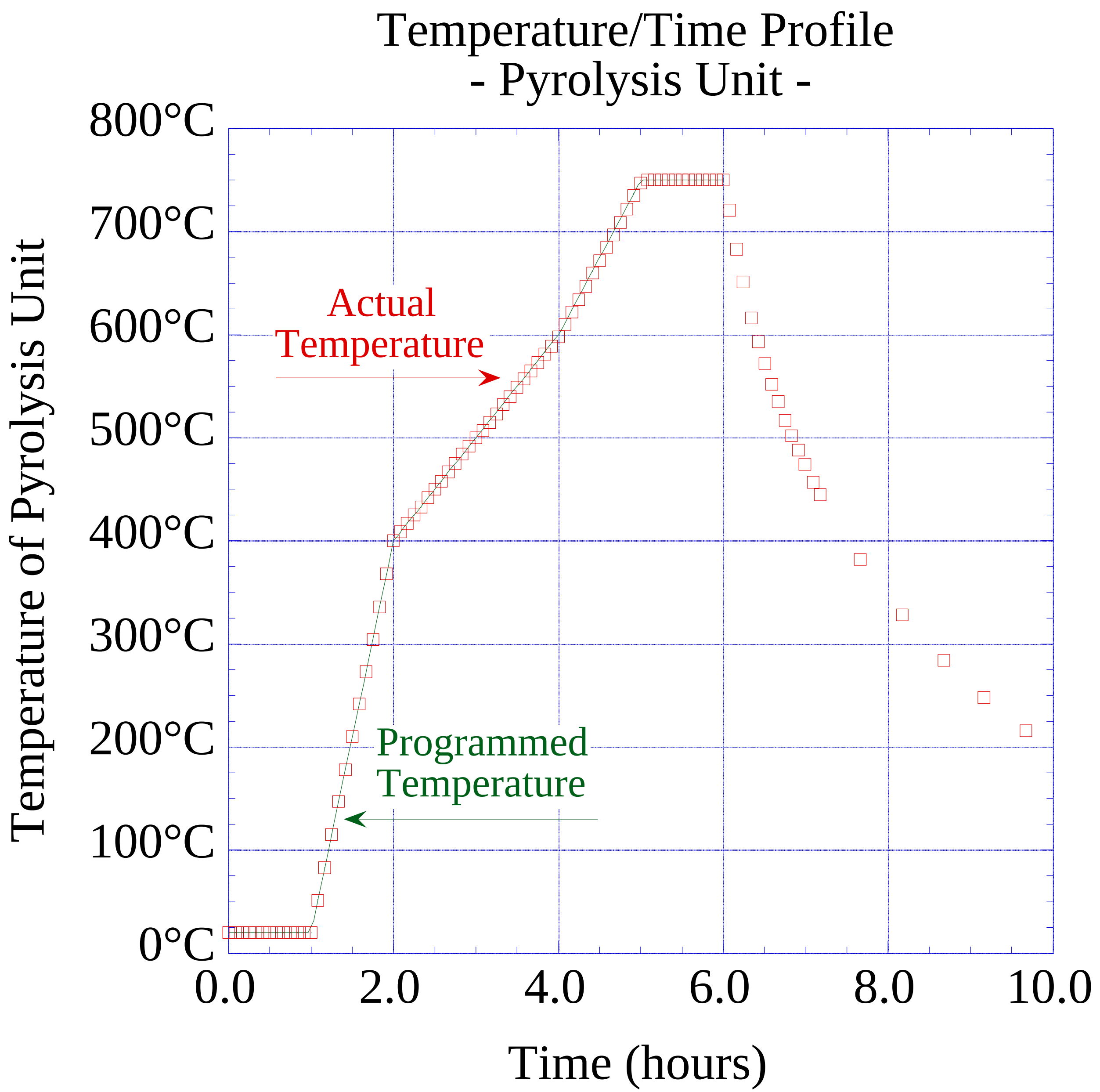
The Pyrolysis Unit



- Design advantages:
  - It is user-friendly for glovebox operations.
  - It minimizes actinide entrainment.
  - It requires only minimal maintenance.

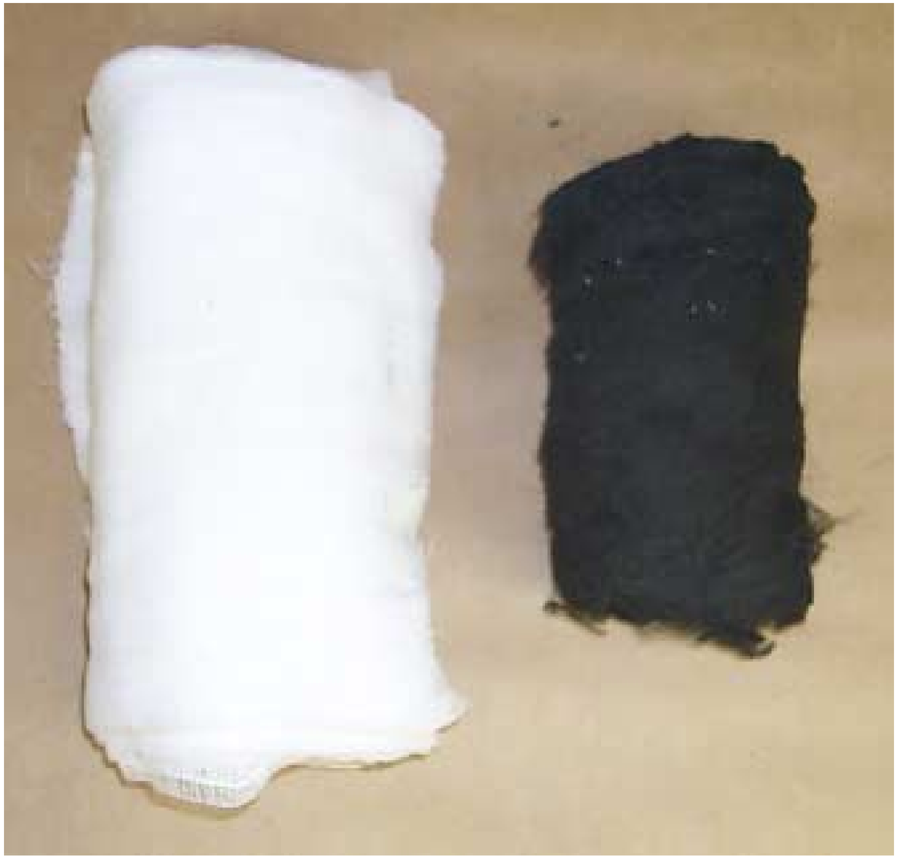
The Pyrolysis Unit

- Approximately 150 grams of cellulose are placed in the reactor insert. The insert is lowered into the reactor, and the reactor is sealed.
- Argon flow is initiated. The pyrolysis unit is then brought to elevated temperatures to decompose the cellulose.


Temperature/Time Profile
- Pyrolysis Unit -
800°C
700°C
600°C
500°C
400°C
300°C
200°C
100°C
0°C
0.0
2.0
4.0
6.0
8.0
10.0
Time (hours)
Temperature of Pyrolysis Unit
Actual
Temperature
Programmed
Temperature

The Performance of the Pyrolysis Unit

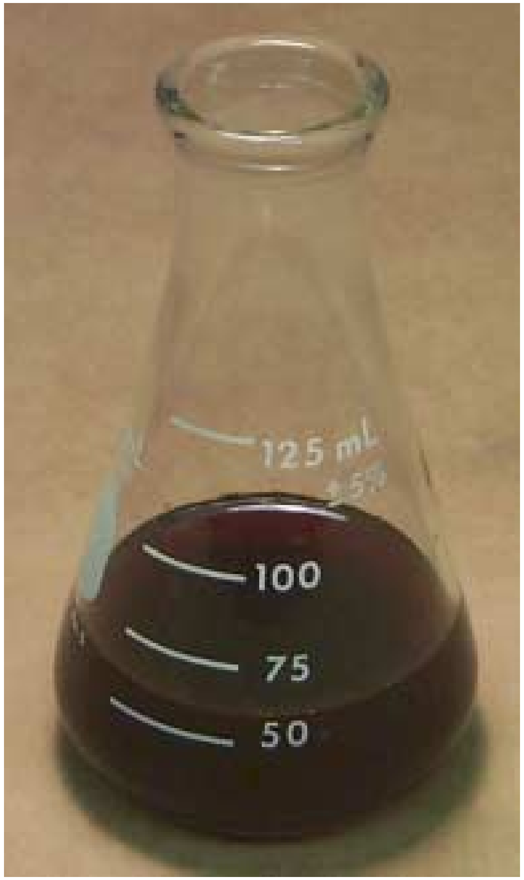
Dry Solids Left in Reactor after Pyrolysis



- Composition of dry solids:
  - The dry solids are predominantly carbon.
- Total mass = 31.3 grams. (Mass reduction = 79.1%)
- The actinides are later recovered using conventional separation and purification processes.

The Performance of the Pyrolysis Unit

Condensable Fraction of the Reactor Off-Gas



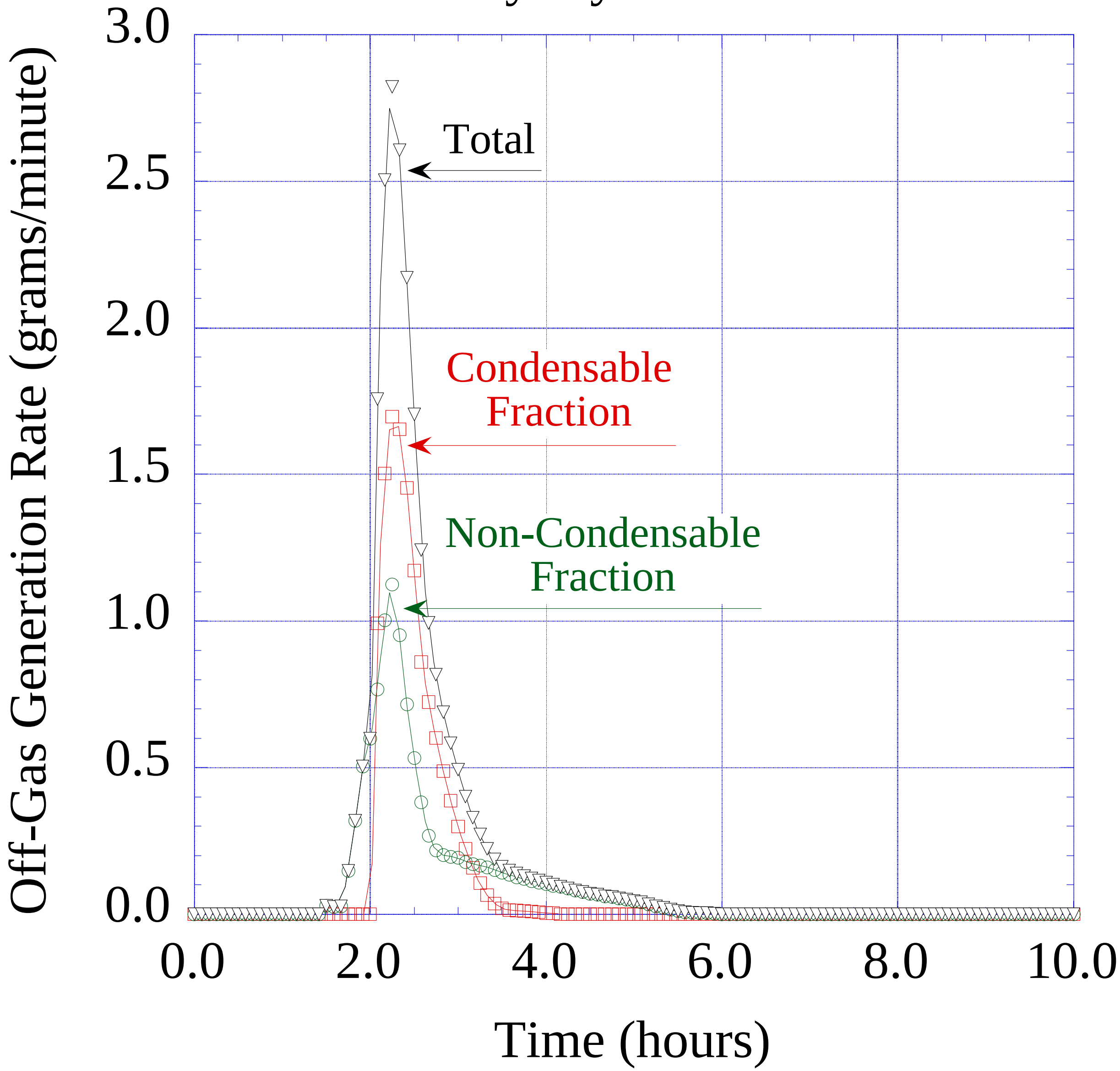
- Composition of condensable fraction:
  - Water: 13.7%
  - Alcohols, aldehydes, etc.: 40.0%
  - Saccharide cmpds.: 13.7%
  - Pyrolytic lignin: 23.6%
  - Particulate carbon: 9.0%
- Total mass = 64.3 grams.

The Performance of the Pyrolysis Unit

- Composition of non-condensable fraction:
  - > CO_2: 4.6%
  - > CO: 5.2%
  - > C_1 - C_3 hydrocarbons: 0.8%
  - > Other compounds†: 89.4%
- Total mass = 54.4 grams.

† The other compounds in the non-condensable fraction consist of volatilized and colloidal versions of the compounds found in the condensable fraction.

Off-Gas Generation Rates
- Pyrolysis Unit -



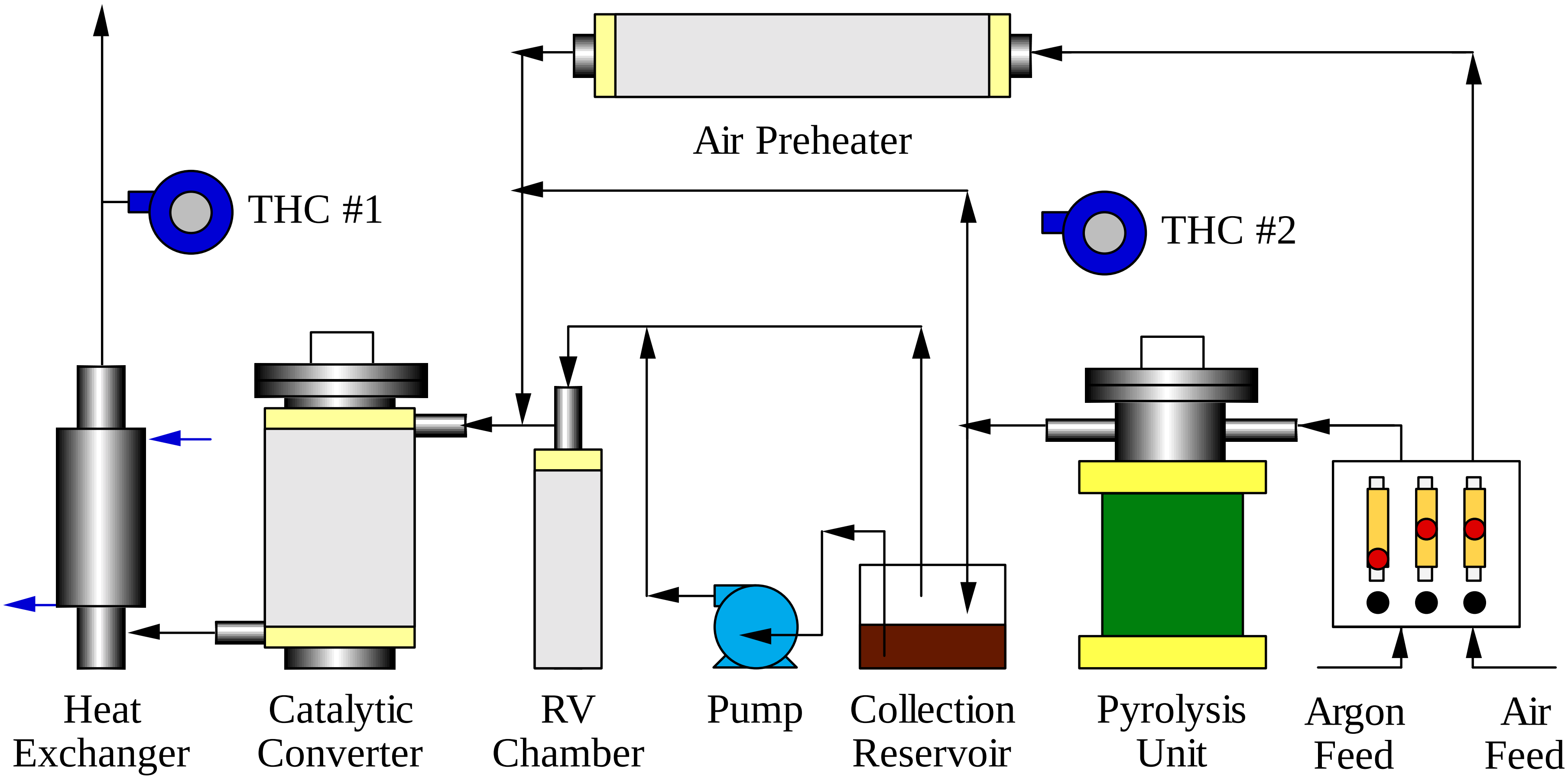
The Performance of the Pyrolysis Reactor

- Problem: When stabilizing 150 grams of cellulose, the pyrolysis reactor generates off-gas at a maximum rate of 2.8 grams/minute. Designing a catalytic converter to oxidize the off-gas at this rate presents two problems.
  - Heat generation: Oxidation of hydrocarbons is highly exothermic. The resulting high temperatures would damage the catalytic converter.
  - Size limitations: A catalytic converter designed to oxidize the off-gas at 2.8 grams/minute would be too large to fit in a standard glovebox.

The Performance of the Pyrolysis Reactor

- Solution:
  - > The non-condensable fraction of the off-gas is processed by the catalytic converter as soon as it exits the pyrolysis reactor.
  - > The condensable fraction of the off-gas is collected in a reservoir, and is processed at a later time.
  - > Processing the non-condensable and the condensable fractions at different times minimizes the size of the catalytic converter, and enhances its overall performance.

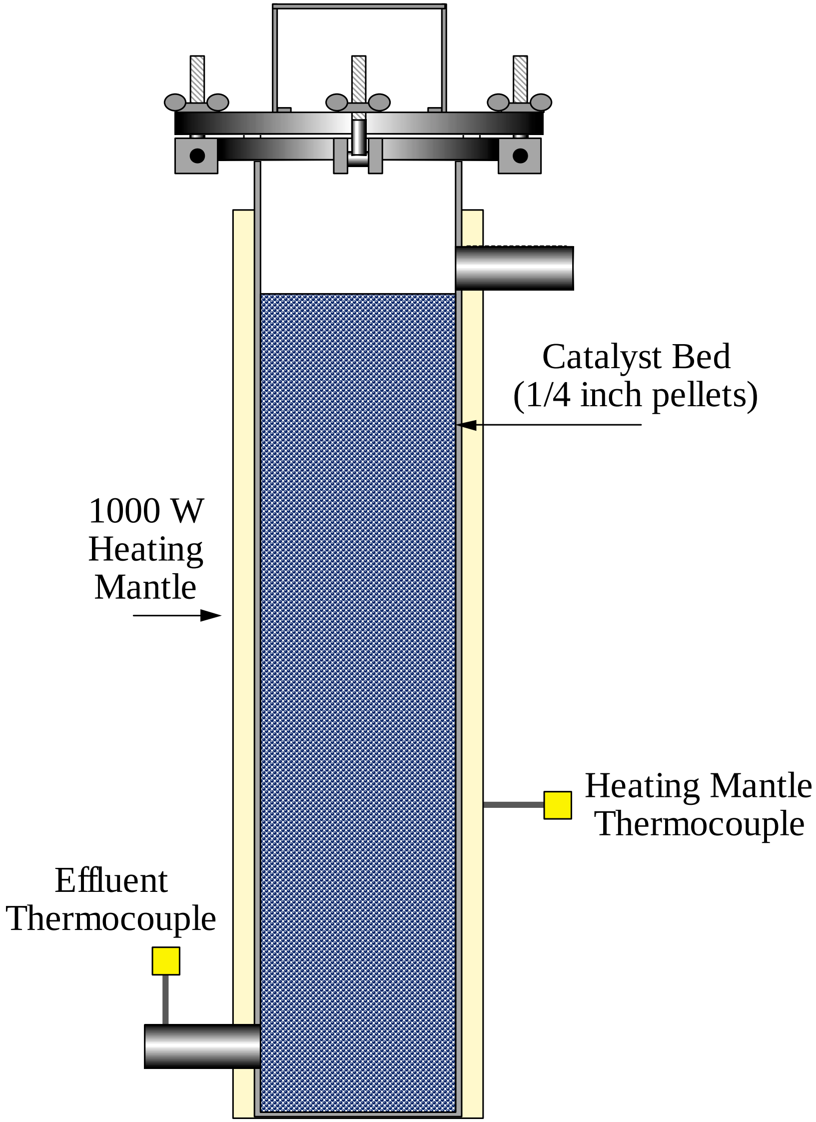
The Pyrolysis Process with Catalytic Conversion



The Catalytic Converter

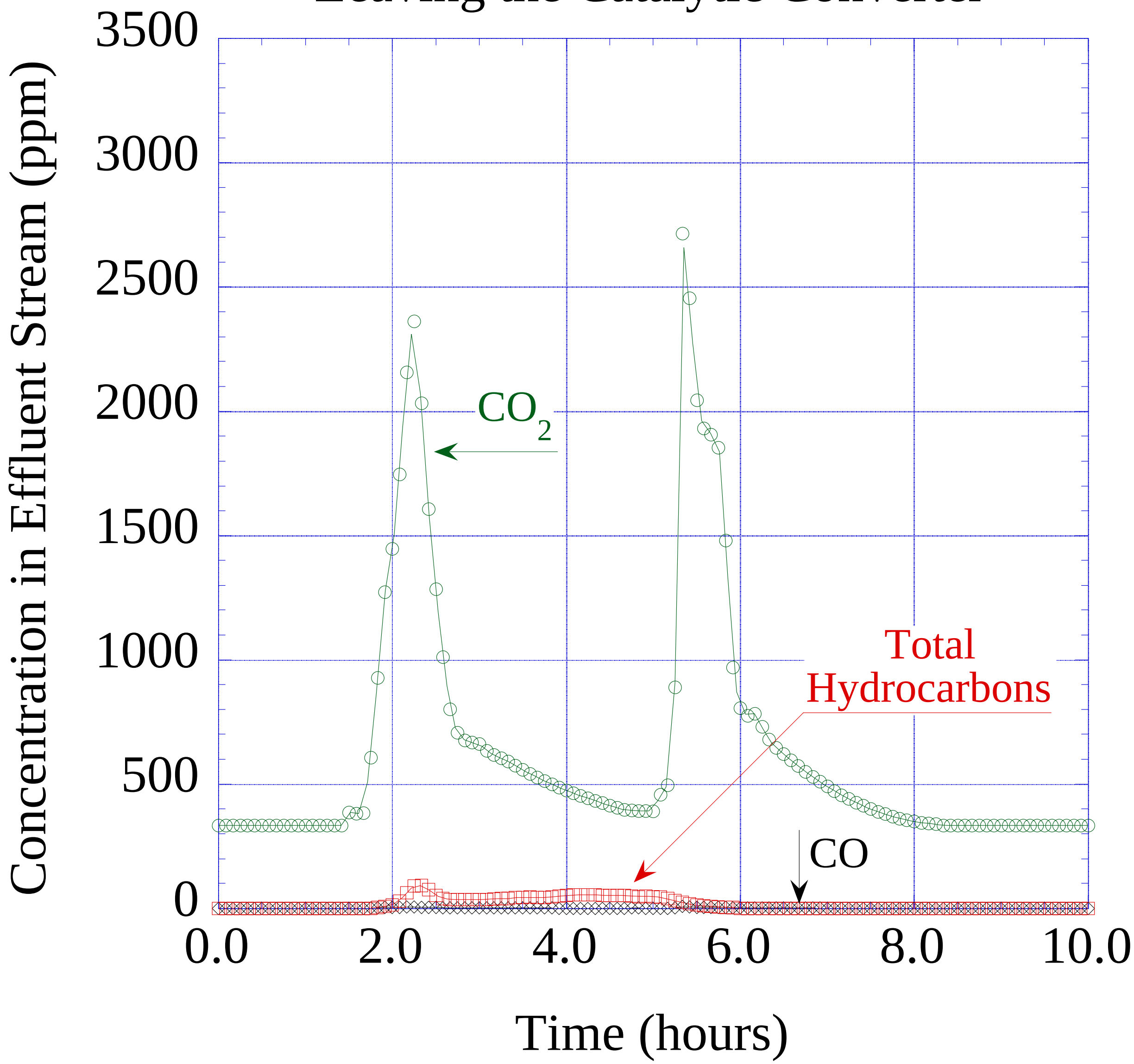
- The catalyst used in the process is the PRO*HHC VOC catalyst provided by Prototech Company.
  - It is a precious metal catalyst designed to be resistant to acid gases.
  - The catalyst is in the form of 1/4 inch pellets. This facilitates handling in glovebox applications.

The Catalytic Converter



- Three factors are used to evaluate the performance of the catalytic converter.
  - Oxidation efficiency
  - Selectivity
  - Catalyst longevity

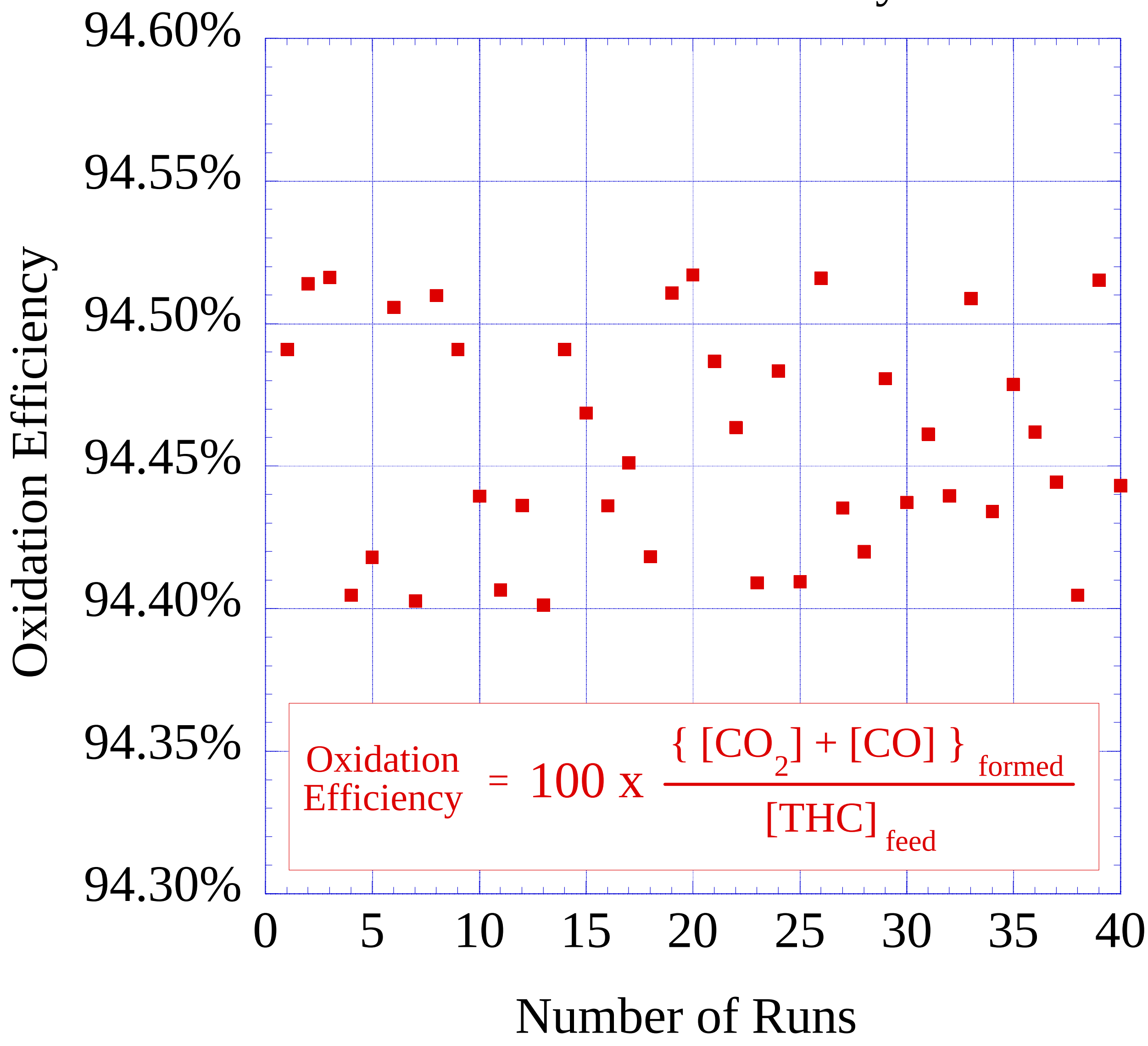
Composition of Effluent Stream Leaving the Catalytic Converter



The Performance of the Catalytic Converter

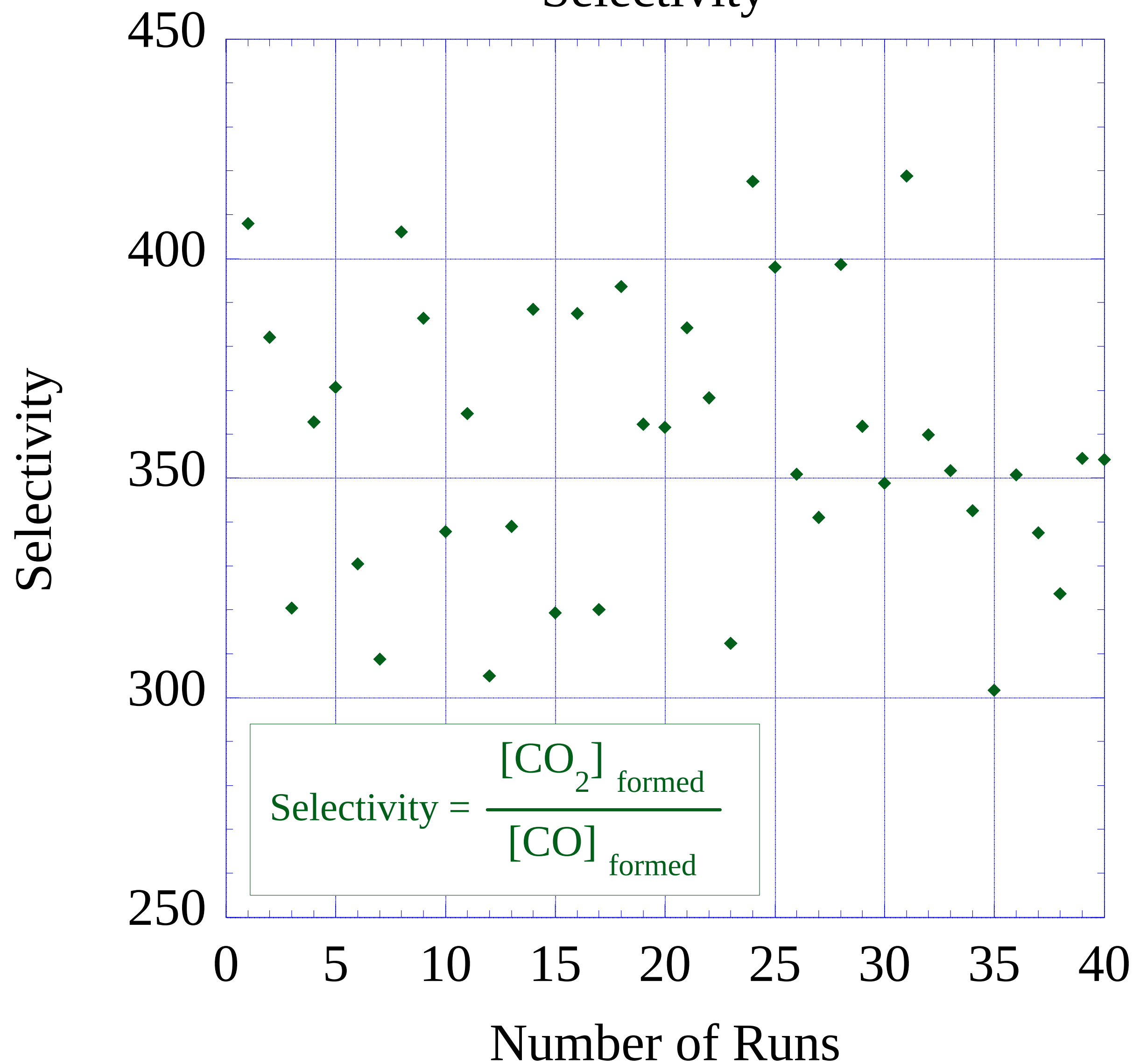
- Oxidation efficiency:
  - The overall oxidation efficiency of the pyrolysis process with catalytic conversion is greater than 94%.
  - Virtually all of the hydrocarbons are oxidized.
- Selectivity:
  - The $[CO_2]/[CO]$ selectivity is greater than 300.
  - The catalytic converter not only oxidizes the hydrocarbons, it oxidizes them completely to CO_2.
- The catalytic converter eliminates the need for a scrubber, and effectively mitigates any combustible hazard.

Catalyst Longevity Tests
- Oxidation Efficiency -



$$\text{Oxidation Efficiency} = 100 \times \frac{\{[CO_2] + [CO]\}_{formed}}{[THC]_{feed}}$$

Catalyst Longevity Tests
- Selectivity -



The Performance of the Catalytic Converter

- Catalyst longevity:
  - For the 40 runs conducted, there was no statistically significant reduction in the oxidation efficiency or the selectivity of the catalyst.
  - The catalytic converter can operate for an extended period of time without the catalyst needing to be replaced.

The Computer Control System

- <u>The computer control system</u>:
  - > The computer control system uses state-of-the-art Allen-Bradley hardware and Intellution software.
  - > It facilitates the operation and maintenance of the process.
  - > It automatically shuts down the process if it deviates from its normal operating parameters.